PREPARATION AND CHARACTERIZATION OF A SEMICONDUCTING OXIDE GLASS THICK FILM BY QUICK QUECHING

PROJECT REPORT SUBMITTED IN PARTIAL FULFILMENT OF REQUIREMENT FOR THE AWARD OF THE DEGREE OF

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SWAGATIKA BISWAL

Roll No.-412PH2090

Under the supervision of

Prof. B.K Choudhuri

National Institute of technology, Rourkela

769008

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA

DEPARTMENT OF PHYSICS AND ASTRONOMY

CERTIFICATE

This is to certify that the thesis entitled, **"Preparation and characterization of a semiconducting oxide glass thick film by Quick quenching"** being submitted as 1 year training report for fulfilling the requirements for the award of the degree of Masters of Science in physics of the **National Institute of Technology, Rourkela**, is a faithful record of bona fide research work carried out by **Miss. Swagatika Biswal** under the supervision of **Prof B.K Choudhuri, Visiting Professor,** NIT, Rourkela and that no part of this thesis has been submitted for any other degree or diploma or published in any form. It is further certified that the assistance and help availed of during the course of the study have been duly acknowledged.

(Prof. D.K Bisoyi) | **(Prof. B.K Choudhuri)**

HOD, Physics Dept. | **Visiting Professor, Physics Dept.**

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Swagatika Biswal
412ph2090

ABSTRACT

We have thoroughly investigated the current status of semiconducting oxide glasses used in technological and biomedical applications. Conductivity of the transition metal oxide glasses appears due to Mott's polaron hopping conducting mechanism. But most bioactive glasses are non transition metal oxide glass and insulators. In this project we have selected an interesting composite glass viz. V_2O_5-HAP [$Ca_{10}(PO_4)$ $(HO)_2$] which is found to be both semiconducting and bioconducting (bioactive).To improve conductivity and hence bioconductivity, we have also added Ag (remained in the glass as nanoparticles). We have characterized the samples from the XRD, FTIR and DTA studies. We have also measured the frequency dependent electrical conductivity and dielectric constant of these glasses. These glasses may find its applications in electronic devices (as a semiconductor) and in water purification and in biomedical application (as a bioconducting material).

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CHAPTER 1

1. INTRODUCTION

GLASS is to be considered very old substance prepared by ancient mankind more than several thousand years ago. Probably in the 18^{th} century manufacturing of and making glass pots .It was started in Egypt. Early glass was similar to present day sode -lime-silica glass. At the beginning the knowledge of science probably did not partial glass production to a great extent. It started in the present century mostly by the investigators Scheele and Lavoisier. They worked on the durability of glass in presence of water and dilute acids. Harcourt and Faraday worked on the production and properties of different types of glass systems.

The cost of glass as a laboratory substance is very lare. Workers can make composite glass equipment using simple instruments; and probably of even lare cost in research is the simplicity with which compound glass instruments can be modified. And also added with little changing. Glass is chemically quite inert for many uses, and vitreous SiO2 may be used when extra- ordinary importance was given. The clearness of glass is always very important. This indicates glass is a good insulator electrical.

1.1 WHAT IS GLASS?

Glass is a substance and it has highly disordered molecular structure. Glass is formed by when the melt is quickly quenched. Crystalline phase and amorphous phase are considered to be the two phases of solid substances. All glasses are typically amorphous solid substances and they show glass transition temperatures (Tg). This transition is reversible for an amorphous substance from a hard state into a rubber like state. They are optically clean also brittle. Sand and other minerals are melted together at a very high temperature to form glass. They produce materials starting from packaging, construction, to finite optical glasses and lenses. Glasses consisting mainly silica (SiO_2) are called silicate glasses. The crystalline form of SiO_2 is known to be quartz. When some impurity, elements, compounds etc. are added to the SiO2 glass while melting, we get coloured glass. Their properties are also quite interesting. Glass may also contain inorganic compounds, glass may also be an organic polymer, plastic, also may be an aqueous solution. Naturally glass may form in the mouth of volcano. Glass looks like liquid. At room temperature it is viscous that appears like a solid. At higher temperature glass gradually softens. This softening character of glass helps to make blown to different shapes and sizes.

Figure 1: shows the picture of glass

1.2 STRUCTURE OF GLASS

The random network model of glass in which the nature of bonding in the crystal is identical to glass. But the essential structural units in glasses are associated in a random manner from the periodic structure of crystals. The structure of glasses is determined by diffraction and spectroscopic techniques. There is absence of long range order in glasses and amorphous materials. The short range order of glass produced from different substance bonding and interaction dynamics. Covalent glasses are loosely packed, with powerfully bound network structures. Random network structure of glass is a very important. The bonding structures of glasses are disordered, but have the same symmetry showing crystalline behaviour of substances. Network former substances help to form glass they are oxide materials. The common example of silica glass is shown below.

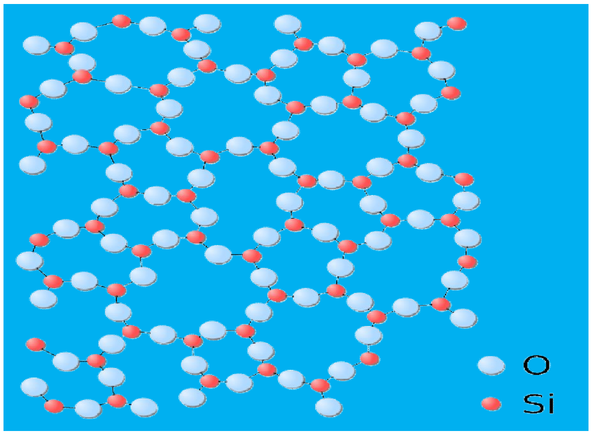


Figure 2: Random network arrangement of SiO_2 silica glass

1.3 PROPERTIES OF GLASSES

Glass is highly viscous solid whose viscosity changes with time. Non transition metal and non rare earth metal oxide glasses are naturally colour less. But transition metal oxide makes the glass coloured. There are various properties of glasses are mentioned below.

1. Chemical stability

As the atoms are oxidized glasses are unaffected to oxidation. Glasses are cosists of mainly 100 %silica tetrahedral i.e. particularly inert. It is attacked by strong alkalis.

2. Weight

Glass is heavy even in relatively small physical sizes. And the density of the glass is 2,500 kg /C^3 approximately 2.5 times heavier than volume of water. The weight of glass identifies the window frames and the structural elements used to specially design for the glazing role.

3. **Conductivity**

Conductivity is the ability of a material to conduct electricity which dependent upon the presence of electrons in the conduction band .Glass is a very poor conductor of electricity and also a poor conductor of heat. Thus, hot glass may be crack when cold water is poured onto it surface. The thermal conductivity of a standard glass is used in coating technology and double glazing. Transition metal oxide glasses are semiconducting.

4. **Light Transmission**

Normally glass is not completely clear but only some of visible light to pass through it. Because the wave-length of light moves away from the visible range is quite opaque. Almost glass is made for viewing objects and used for light transmission. Glass is transparent to short wave infra-red but opaque to long-wave infra-red. Light transmission varies with dissimilar type of glass with different thickness.

5. **Temperature Performance**

Glass is formed at high temperature and returns to liquid state after sufficient heating. These glass products are used for fire protection of substrates, laminates and other technologies product. The temperature of glass is not high but thermal endurance. So glass products are non-breakable whose temperature is 250 degrees.

6. Strength

Glass is harder than steel and elastic in nature. Due to strong bonding between the atoms glass has very high compressive strength and the measured theoretical strength is about 107 kg N/m^2. As the molecular structures in glass are incapable to move, so the ordinary glass will crack.

7. Thermal expansion behaviour and stress

Normally one part of glass will be joined with other glasses or other types of different materials to form the final product which signifies the thermal expansion behaviour of the material. Difference in thermal expansion between the two glasses will produced stress in the fasten region. The stress can be measured by optical birefringence.

1.4 GLASS TRANSITION TEMPERATURE

The glass transition is the reversible transition in amorphous materials from a hard and comparatively brittle state into rubber-like state. Amorphous exhibits a glass transition temperature is called as glass. When a liquid is molecule is cooled in 100^{0}C bellow its equilibrium crystalline melting temperature (Tm) glass will be formed. The temperature at which the glass transition occurs is called as the glass transition temperature (Tg). Above the glass transition temperature (Tg), the system is in rubbery state and bellow glass transition temperature (Tg), the system is in the glassy state. According to thermodynamics glass transition show second order transition which does not happen immediately. The glass transition temperature is based on Gibb’s free energy. Time & temperature both are exchangeable quantities when dealing with glass.

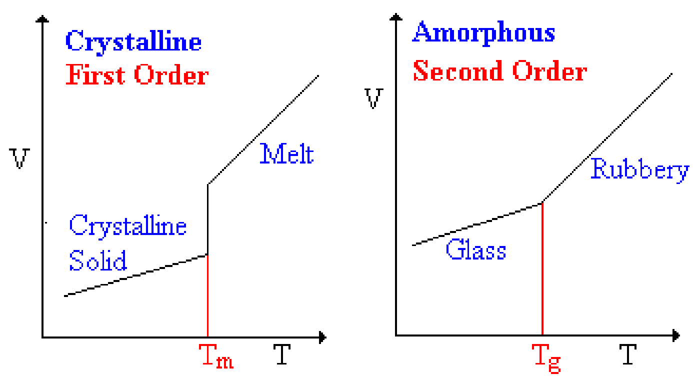


Figure 3: Glass transition temperature of normal glass

1.5 TYPES OF GLASS

Different types of glass are formed due to the ingredients and the method of manufacture. So the different types of glass show different type of properties and uses.

1. Soda-lime glass

It is the known variety of glass and is manufactured by heating sodium carbonate and silica. And used for making windows glass, bottles and electric bulbs.

2. Optical glass

Optical glass is softer and transparent. It is also called flint glass used in manufacture of lenses, prisms and other optical instruments.

3. Borosilicate glass

Borosilicate glass is made up of silica and boric oxide with little amounts of alkali and aluminium oxide. This glass show chemical durability and thermal resistance means it doesn't break with rapid varying temperature. It is basically used in pharmaceutical sector, chemical industry and a mixture of high intensity lighting.

4. Bioactive glass

Bioactive glass show amorphous structure consist element like silicon, calcium, sodium, phosphorous and oxygen which is found in our body. Many decade of researchers found that bioactive glasses are mostly biocompatible. Bioactive glass releases ions when activated with water as they acquire a very high bioavailability. Bioactive glass used in cosmetics and human body.

5. Metallic glass

Metallic glasses are made up of alloy and show disordered atomic structure. When metals are crystalline in solid state show ordered arrangement of atoms but when metals are non-crystalline show glass like structure. Essentially metals are good conductor of electricity. Metallic glasses are produced in various ways like rapid cooling, physical vapour deposition, rapid cooling, solid-state reaction, ion irradiation, and mechanical alloying.

6. Semiconducting Glass

The electrical properties lies in between conductor and insulator are called semiconductor. Semiconducting glasses shows lowest thermal conductivities, lowest electrical conductivity and low mobility. Semiconducting chalcogenide glasses are used as raw materials. Rare earth metal oxide glasses and transition metal oxide glasses show Semi conductivity due to mixed valance state. Semi conductivity arises due to hopping of electron from higher valance state to lower valance state.

For our present thesis work we chose a novel transition metal oxide glass called vanadate glass composed of V_2O_5 and hydroxyapatite viz. $Ca_{10}(PO4)_6(HO)_2$. This glass is semiconducting and also biologically active. My aim is to prepare, characterize and study of some physical properties of this glass. I have also introduced Ag nanoparticles to improve its conductivity.

CHAPTER 2

2.1 STUDY OF SEMICONDUCTING VANNADATE GLASS WITH HAP

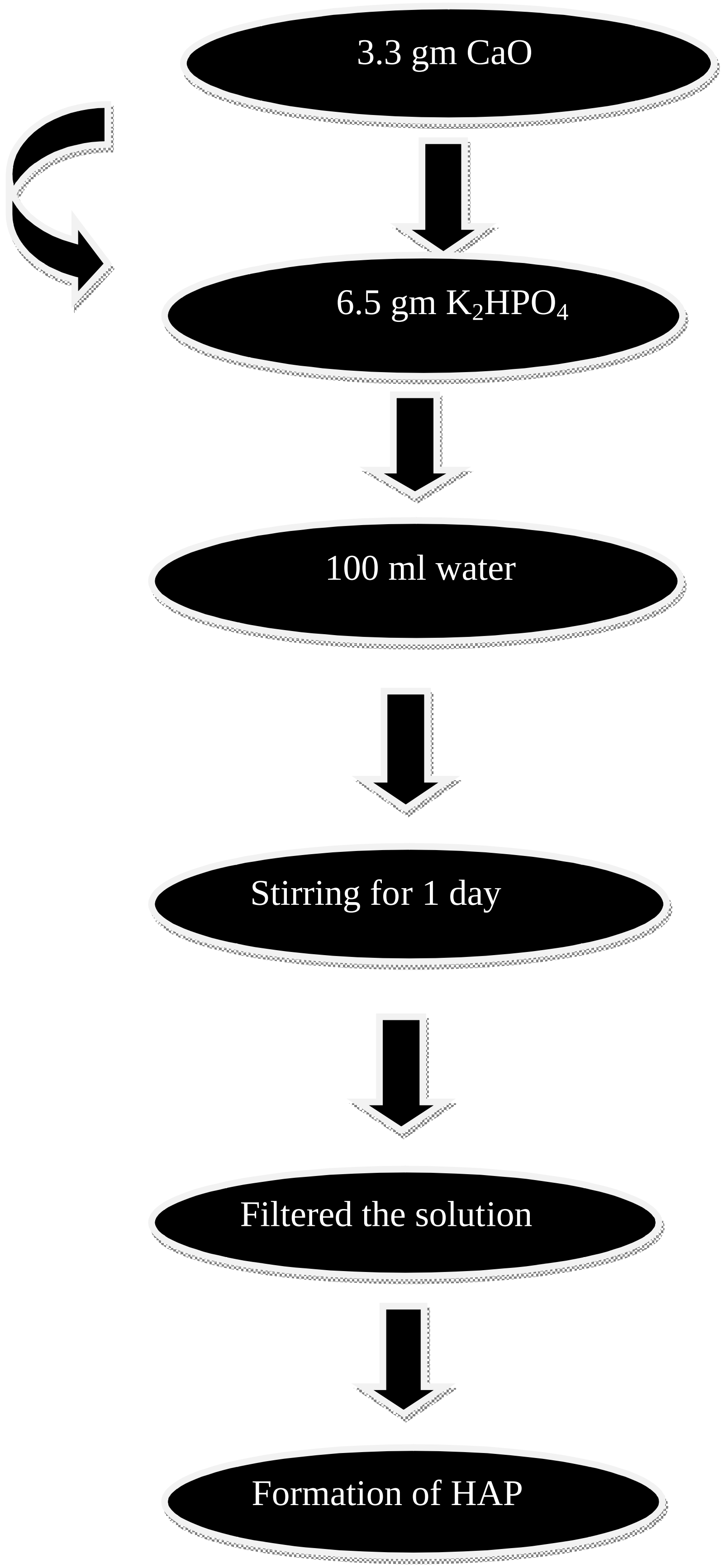
Transition metal oxides form homogeneous glass with glass former like B_2O_3, Bi_2O_3 etc. Here strong electron phonon interaction is responsible for polaron formation. Hopping of polarons causes semiconductiviy in these glasses. These semiconducting glasses are useful for many technological applications like capacitors, sensors etc. Recently some transition metal oxide glasses are found to be both semiconducting and bio conducting (i.e. biologically active). Hydroxyapatite (HAP) with chemical formula $Ca_{10}(PO_4)_6 (HO)_2$ is a well recognized bio ceramic material. The transition metal oxide (TMO) glasses formed with HAP are both semiconducting and bioactive. Bioactive glasses are important for water purification and also medical applications. In our laboratory HAP has been synthesized from egg shells. We have prepared V_2O_5-HAP glasses which are semiconducting and bioactive. We have also added little silver to make these glasses more conducting and more bioactive. Because, it has been reported earlier that increase of conductivity in oxide ceramics improves bioactivity of the ceramics.

2.2 MATERIALS USED

V_2O_5, HAP ($C_a (PO_4)_6(HO)_2$), A_gNO_3, CaO (from egg shell) , K_2HPO_4

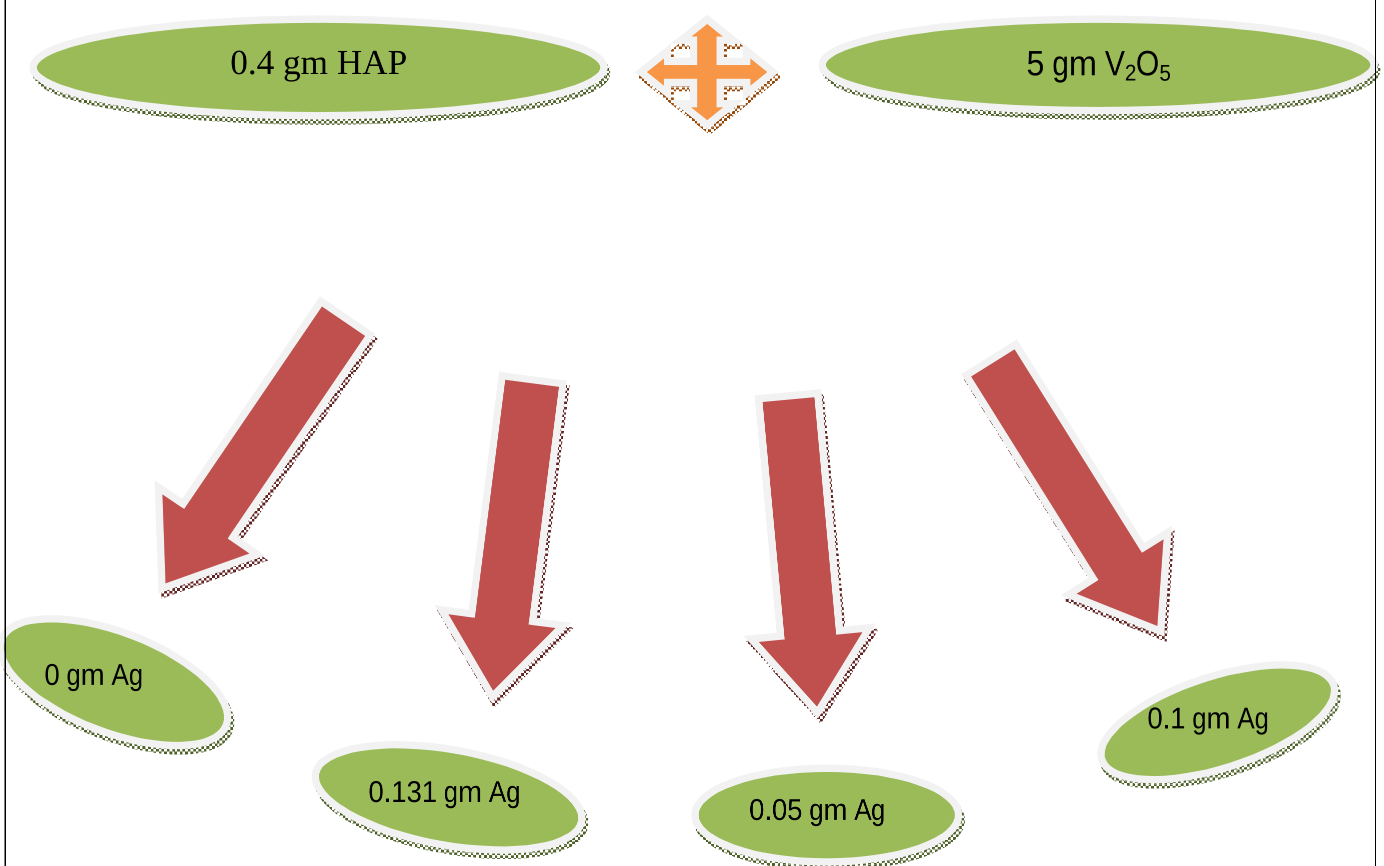
2.3 PREPARATION OF HAP

In order to prepare the HAP solution 3.3 gm of CaO was weighed out in a beaker and 6.5 gm of K_2HPO_4 was taken in another beaker. Then both of the solution was dissolved in 100 ml of water. The solution was stirred for 1 day and kept for another day at 37^oC. After that the mixture was filtered and washed several times to obtain pure HAP.


3.3 gm CaO
6.5 gm K_2HPO_4
100 ml water
Stirring for 1 day
Filtered the solution
Formation of HAP

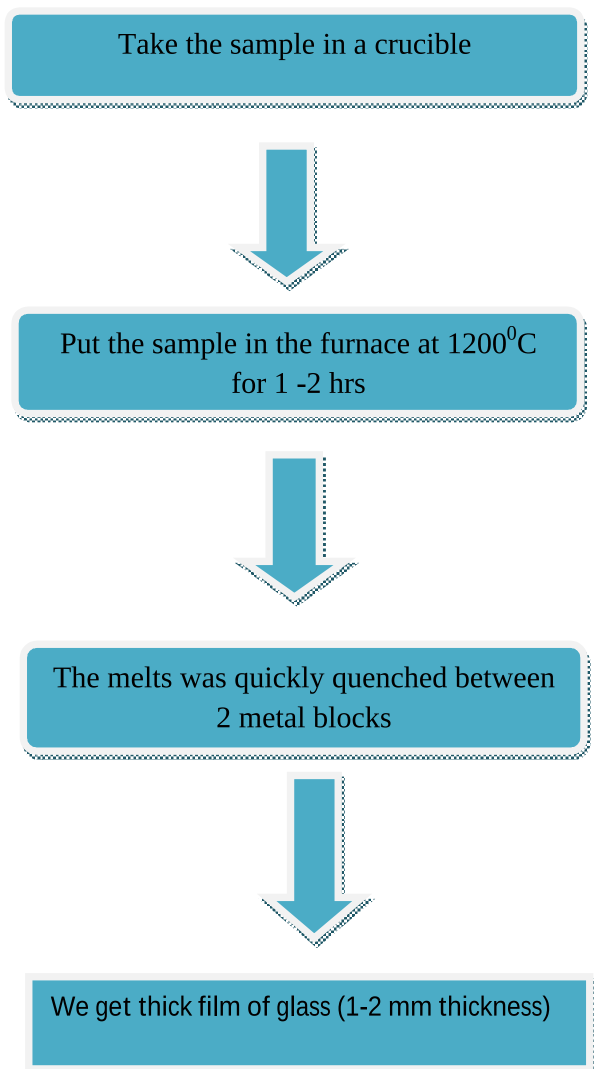
2.4 PREPARATION OF GLASS POWDER SAMPLES

After the preparation of HAP, 0.4 gm of HAP was weighted out and added to 5gm of V_2O_5 without adding silver. In this way 4 samples was prepared with 0.0131 gm of $AgNO_3$, 0.05 gm of $AgNO_3$ and 0.1 gm of $AgNO_3$..



2.5 PREPARATION OF V_2O_5-HAP-Ag GLASSES

The 4 samples were taken in an alumina crucible then put the samples in a furnace at 1200^0c for 1-2 hrs. A melts was formed and quickly quenched between two metal blocks. After that we get a thick film of glass I.e. 1 to 2 mm thickness or less than that.



CHAPTER 3

CARACTERIZATION TECHNIQUES

3.1 X-RAY DIFFRACTION (XRD)

X-rays is an electromagnetic radiation. When a monochromatic beam of radiation falls on the crystal then the rays are diffracted through the crystal. The rays are known called x-ray. X-ray diffraction is used to study and figure the crystalline nature of materials and the diffraction planes of atoms within the material. It measure the wavelength around angstroms level to nm level. The incident X-ray has same order of wavelength as that of the atomic dimensions hence the radiation emitted by an electron in common is phase with each other. This principle was done by Bragg's law. According to Bragg's law

2? ? ??? = ? ?

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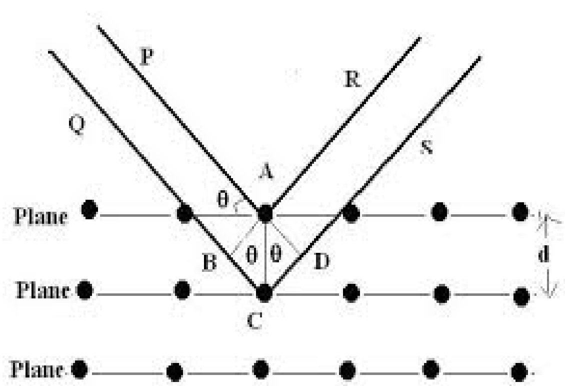

Figure 4: Diffraction through crystal planes

Finally we found that X-ray diffraction has become a very important for structure and characterization of crystal.

3.2 DIFFERENTIAL THERMAL ANALYSIS (DTA)

Differential thermal analysis (DTA) is a technique in thermodynamic which is same as differential scanning calorimetry (DSC). Here the material property was studied by temperature difference between sample and reference. In DTA the graph is plotted differential temp against the time and temperature and the sample changes to either exothermic or endothermic. DTA data shows the glass transition, crystallization, melting and sublimation.

Figure 5: instrument for DTA

3.3 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR stands for Fourier Transform infrared spectroscopy. It is a mathematical process which very commonly expresses a function of time as a function of frequency. Here the whole spectrum was recording within a very short periods of time. From the physics point of view, several electromagnetic frequencies when added give rise to an interference pattern. This method converts a time domain plot into frequency domain plot/spectrum. For about 2 seconds, the detector records about 2000 samplings of the complex wave at taking data at every millisecond. Also in this method we know the band structure of molecule and the vibration motion the molecule.

Figure 6: instrument used for FTIR

3.4 DIELECTRIC MEASUREMENT

Dielectric is an electrical insulator when an electric field is applied to it becomes polarized. When a dielectric is placed in an electric field then electric charge does not flow through the material but shifted slightly from their equilibrium position. The molecules are not polarized if a dielectric is composed of weakly bonded molecules. In dielectric a graph is plotted dielectric constant against frequency. Dielectric constant is specially used in optics, solid state physics and electronics.

Figure 7: instrument used for measuring dielectric constant

3.5 CONUCTIVITY MEASUREMENT

Conductivity of a substance is the ability or power to conduct electricity and heat. Its unit is seimens per meter. For conductivity measurement a graph is plotted conductivity against frequency and the conductivity was found from the dielectric constant. Conductivity is the reciprocal of resistivity.

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CHAPTER 4

RESULTS AND DISCUSSION

4.1 Structural analysis by XRD of glas

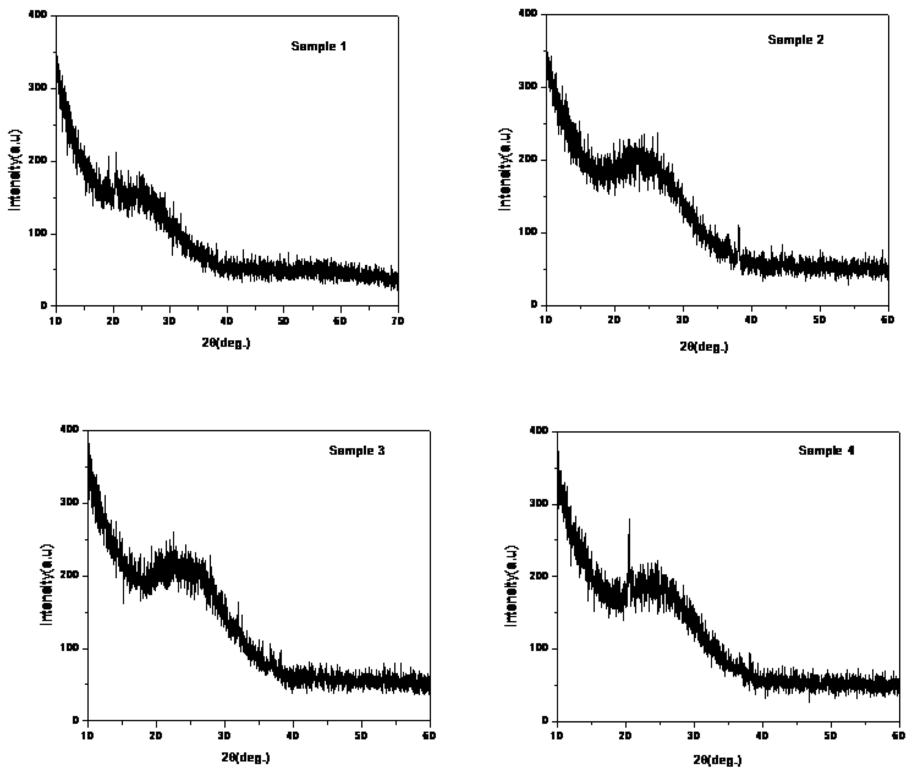


Fig.8 shows the XRD data of 4 vanadate glass samples

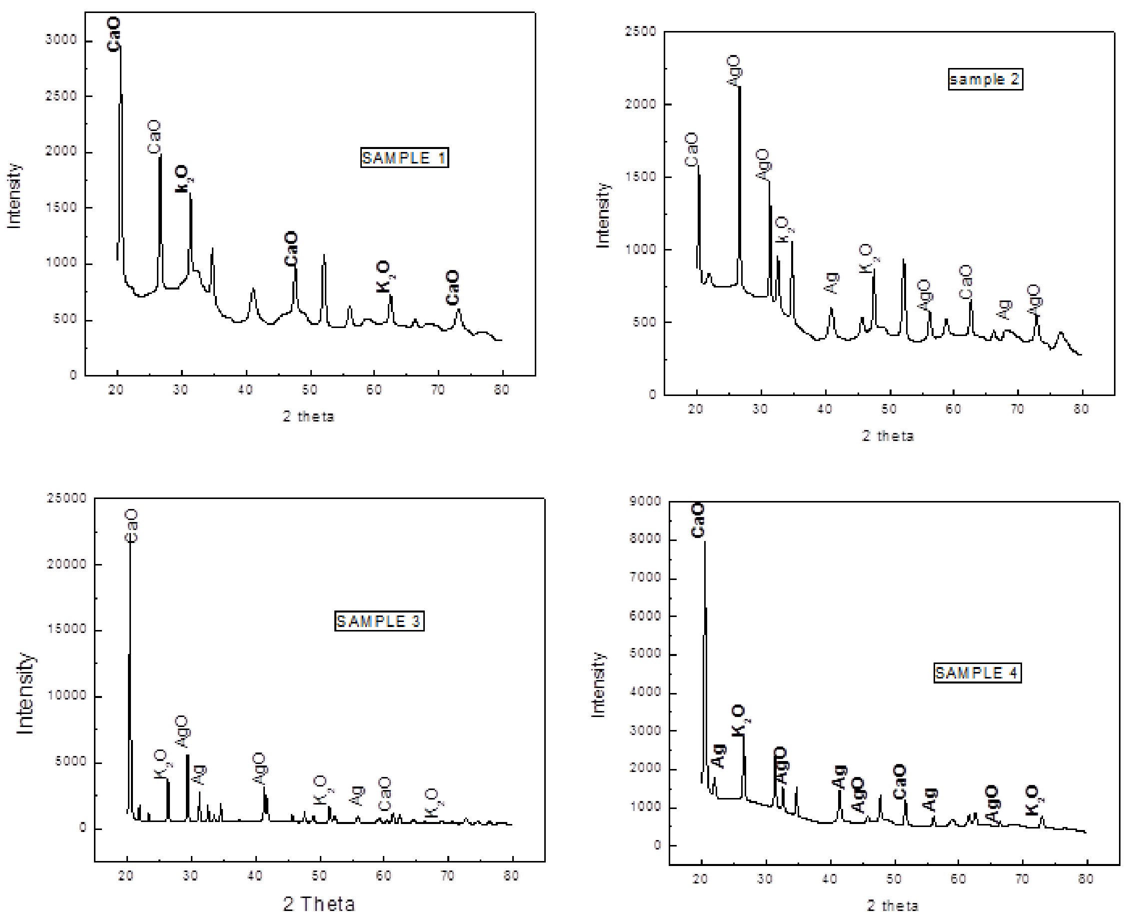
Figure 8 shows the XRD of the four glasses with different concentrations of Ag. XRD indicates amorphous character of the samples showing no peak. This means homogeneous non- crystalline glasses have been formed.

Glass Sample 1: V_2O_5 (5g)-HAP (0.4gm)-AG (0gm), Glass Sample 2: V_2O_5 (5g)-HAP (0.4gm)-$AgNO_3$ (0.0131gm),

Glass Sample 3: V_2O_5 (5gm)-HAP (0.4gm)-$AgNO_3$ (0.05gm)

Glass Sample 4: V_2O_5 (5gm)-HAP(0.4gm)-$AgNO_3$(0.1gm).

To study the effect of annealing the glass we have annealed the glasses at two different temperatures (300 ^oC and 400^0C), one near the glass transition temperature Tg and the other little above the glass transition temperature.



The XRD patterns of the annealed glass samples (1-4) are shown in Figure 9 (for 400^0C annealed sample).

The XRD peak also showed the presence of metallic silver Ag which is in the nano particle forms. Here a transition from non-crystalline amorphous phase to crystalline phase occurred showing the presence of many oxide phases.

4.2 DTA Analysis

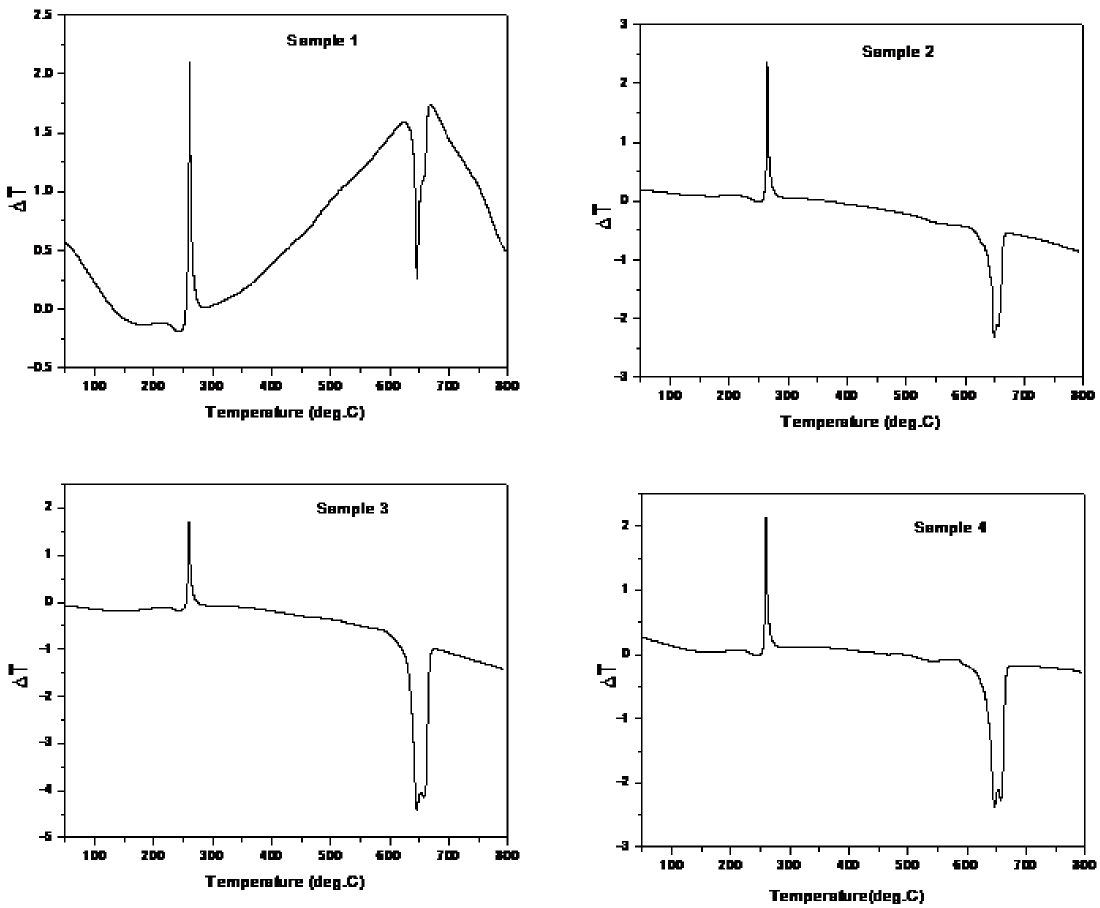


Figure 10: shows the DTA data of 4 glass sample

From these curves we estimate the glass transition temperature and melting temperature of the glasses as shown in Table-1.

Sample no	Glass transition temp (Tg)	Melting temp (Tm)
1	260^0c	660^0c
2	250^0c	650^0c
3	240^0c	640^0c
4	230^0c	630^0c

Figure 10 shows the DTA curves where clear indication of the glass transition temperature and the melting temperature is visualized. Table-1 showed the glass transition temperature and melting temperature of the four glasses. It is observed that with the increase of Ag concentration Tg decreases as well as melting temperature (Tm).

4.3 FTIR Analysis

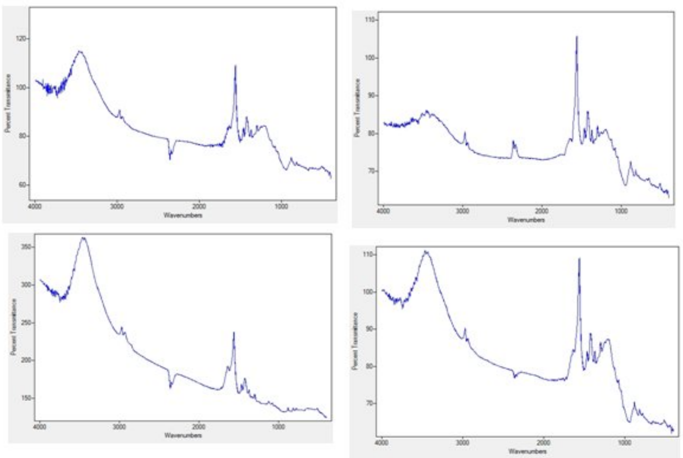


Figure 11: shows the FTIR data of 4 glass samples

Sample-1

Stretching / Bending Mode	Wave Number(cm^{-1})	Functional Group
Symmetric Bending	1563.40039	N-O
Symmetric Stretching	2346.00900	O-H
A Symmetric Stretching	2366.25568	C=C-H

Sample 2

Stretching / Bending Mode	Wave Number(cm^{-1})	Functional Group
Symmetric Bending	1563.404	N-O
Symmetric Stretching	3429.202	O-H
A Symmetric Stretching	3469.695	C=C-H

Sample 3

Stretching / Bending Mode	Wave Number(cm^{-1})	Functional Group
Symmetric Bending	1553.277	N-O
Symmetric Stretching	3439.325	O-H
A Symmetric Stretching	3479.625	C=C-H

Sample 4

Stretching / Bending Mode	Wave Number(cm^{-1})	Functional Group
Symmetric Bending	1556.575	N-O
Symmetric Stretching	3463.465	O-H
A Symmetric Stretching	3433.094	C=C-H

Figure 11 shows the FTIR spectra of four samples .All the glasses show identical feature. Presence of functional groups N-O, O-H, C=C-H are observed in the glass samples.

4.4 Dielectric Measurement

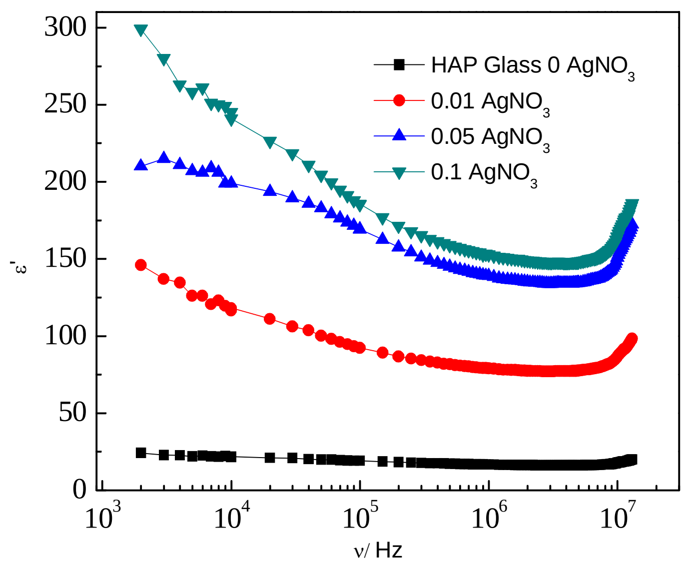


Figure 12: shows the dielectric curve of 4 glass sample

Figure 12 shows the frequency dependent dielectric constant of the glass samples. It is interesting to note that the dielectric constant of the Ag free glass (sample -1) is almost independent of frequency. But with the addition of Ag in the glass dielectric constant increases and also shows frequency dependent behaviour. Ag addition forms micro capacitors which increases the dielectric constant of the glass.

4.5 Conductivity Measurement

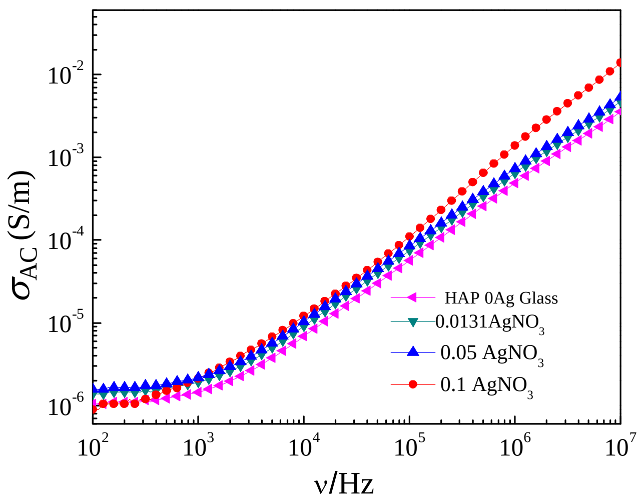


Figure 13: shows conductivity curve of 4 samples

Figure 13 shows the frequency dependent ac conductivity of glasses at room temperature. Here we observe that conductivity of the glasses increases with increase of Ag content in the glass. This is due to the formation of conduction path ways in the glass with the addition conducting Ag. Room temperature conductivity of the glasses is of the order of $3x10^{-6}$ S/m with is of the same order of magnitude of other semiconducting transition metal oxide glass. We heated the last sample-1 around $100^{o}C$ and measured the conductivity which was estimated to be $1.5x10^{-4}$. This also indicated that our glass samples are semiconducting.

Bioactivity of the Glasses:

To study the bioactivity of the glasses we soaked the glass sample -1 to 10mL phosphate buffer solution or $NH_4H_2PO_4$ solution one week at room temperature. Hydroxyapatite [$Ca_{10}(PO_4)_6(HO)_2$] was found to deposit on the glass surface indicating its bioactivity. HAP formed was analysed by XRD and FTIR studies. These studies are being carried out by us.

CHAPTER 5

CONCLUSION

We have prepared four new transition metal oxide glasses by fast quenching technique. We have characterized these glasses from the studies of XRD, FTIR and DTA. We have also measured electrical conductivity and dielectric constant of these glasses showing semiconducting behaviour similar to other transition metal oxide glasses. Because of the formation of micro capacitors, the dielectric constants of the glasses increase with addition of Ag. These glasses are also found to be bioactive. One of the glasses (Sample-1) showed frequency independent dielectric constant. These glasses might be used as electronic materials or as bioactive materials.

REFFERENCES

[1] M. I. Ojovan (2004). "Glass Formation in Amorphous SiO_2 as a Percolation Phase Transition in a System of Network Defects". JETP Letters 79 (12): 632–634. Bibcode: 2004JETPL...79.632O. doi:10.1134/1.1790021.

[2] Alexander Fluegel. "Glass melting in the laboratory". Glassproperties.com. Retrieved 24 October 2009.

[3] Zallen, R. (1983). The Physics of Amorphous Solids. New York: John Wiley. ISBN 0-471-01968.

[4] P. F. McMillan (2004). "Polyamorphic Transformations in Liquids and Glasses". Journal of Materials Chemistry 14 (10): 1506–1512. Doi: 10.1039/b401308p.

[5] R. M. Hakim and D. R. Uhlmann, Physics Chem. Glasses 12, 132 (1971).

[6] EPCOS 2007: Glass Transition and Crystallization in Phase Change Materials. Retrieved on 2012-06-29.

[7] Glass transition temperature, Wikipedia, the free encyclopedia

[8] X-RAY diffraction, Wikipedia, the free encyclopedia

[9] Differential thermal analysis, Wikipedia, the free encyclopedia

[10] Fourier transforms infrared spectroscopy, Wikipedia, the free encyclopedia

[11] Dielectric measurement, Wikipedia, the free encyclopedia

[12] Web.mit.edu

[13] Glass Wikipedia, the free encyclopedia

[14] www.preserved articles.com

[15] glasstalks.com

[16] www. Lehigh.com

[17] www.esb.ucp.pt

[18] www.glucose sextreffnorge.com

[19] A.P. Goncalves, E.B Lopes, J.B Vaney, B.Lenoir, Volume 193, sep 2012, pages 26

[20] www.us.schott.com

[21] www. Britglass.org.uk

[22] www.research.philips.com

[23] www.guardian.com

[24] en.wikipedia.org